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(54) Title: TREATMENT OF METAKAOLIN

(57) Abstract: A method for increasing the brightness of metakaolins comprises bleaching a metakaolin. The bleaching may be carried out using a reducing agent such as sodium dithionite, sodium hydrosulphite, formamidine sulphinic acid, borohydride. The bleached metakaolins are suitable for use in a variety of applications including for use as a pigment additive in a filler or coating composition.



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TREATMENT OF METAKAOLIN

Field of the Invention

5 The present invention relates to methods for increasing the brightness of metakaolins and products obtained from said methods. The present invention also relates to high brightness bleached metakaolins having a low relative density which may be made according to the methods of the present invention. The brightened metakaolins may be used in a variety of applications, including as pigments in paper and polymer
10 products.

Background of the Invention

Calcined kaolins find use in a variety of application compositions including
15 compositions for making paints, plastics, rubbers, inks, sealants, ceramics, cementitious products, paper and coatings. In these applications they impart to the finished products a number of desirable properties such as brightness, opacity, hiding power, strength (in plastics) and friction (in paper).

The major constituent of kaolin is kaolinite, which has the general formula
20 $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$. The process of calcination removes hydroxyl ions. Depending on the conditions used, the chemical change may be partial or total. This is typically determined by controlling the temperature at which calcination takes place. Typically, and depending on the nature of the particular sample, at about 450-650°C, the kaolin undergoes a strongly endothermic dehydration reaction resulting in the conversion to material known
25 as metakaolin. The metakaolin state can be conveniently ascertained by acid solubility testing because the alumina in the clay (from $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is virtually completely soluble in strong mineral acid.

Despite the numerous advantages afforded by the use of calcined kaolins, there are also a number of disadvantages associated with their use. When compared with
30 uncalcined kaolins they are relatively abrasive, which can result in increased wear of web forming screens (wires) on paper making machines, dulling of paper slitter knives, wear of printing plates when they come in contact with coated paper containing fine calcined pigments in the coating formulation, and, in general, wear of any surface that comes in contact with these pigments.

To overcome at least the abrasion problem, it is known to calcine the kaolin pigments at temperatures less than those required to produce pigments generally referred to by those skilled in the art as "fully calcined" pigments and control the calcination temperature so that the kaolin undergoes the characteristic endothermic dehydration reaction mentioned above, and the original kaolinite is only partially dehydroxylated, thus forming metakaolin.

However, it is well known that the brightness of a metakaolin pigment is typically inferior, generally by about 2-3%, than that of fully calcined pigments derived from the same clay calciner feed. Thus, the fully calcined version gives greater brightness, but generally with poor abrasion characteristics and with associated higher operating costs. The metakaolin has generally lower abrasion, but brightness is also generally inferior.

It is known to bleach clays in order to increase their brightness. Typically, kaolin clays are bleached with reducing bleaches such as hydrosulfite salts to provide clay products of increased brightness and value.

It is known that bleaching of calcined clays is ineffective and does not lead to a significant increase in the brightness of the calcined clay. Known bleached fully calcined kaolins and metakaolins are formed by bleaching uncalcined kaolin prior to the calcination step.

Staining of the surface of kaolins is generally considered to be due to the presence of iron-containing species such as hematite, goethite, lepidocrocite and iron-containing gel species. During bleaching of an uncalcined kaolin, such iron-containing species which are present on the surface of the kaolin are thought to be removed through the conversion of insoluble iron (III) species to soluble iron (II) species. However, iron contained in the lattice of the kaolin may be largely unaffected as it is chemically, physically and structurally inaccessible.

A possible reason for why bleaching of calcined kaolins is ineffective is because during the calcination process, at elevated temperatures, the iron diffuses through the crystalline structure of the particles and after cooling is "locked" into the crystal structure of the kaolin particle and is inaccessible during the subsequent bleaching operation.

The present invention is based on the surprising finding that metakaolin may in fact be effectively bleached after its formation, resulting in a metakaolin of increased brightness.

Summary of the invention

In a first aspect, the present invention provides a method of brightening a metakaolin comprising bleaching said metakaolin.

5 Preferably the brightening of the metakaolin results in an ISO brightness increase of at least 0.3 units. More preferably the ISO brightness increase is at least 0.5 units or at least 1.0 unit. Even more preferably, the ISO brightness increase is at least 2.0 units or 3.0 units. Most preferably the brightening of the metakaolin results in an ISO
10 brightness increase of at least 5.0 units. Preferably the method of the first aspect of the invention comprises (a) forming a dispersed aqueous slurry of the metakaolin and (b) contacting a bleaching agent with the slurry formed in (a). The slurry in (a) may be homogenised using any one of a number of standard techniques. Prior to (b) and/or after (b) the pH may be measured and optionally may be adjusted. Preferably, the bleaching agent and slurry are mixed thoroughly. Adjustment of the pH is achieved by the use of
15 any one of a number of standard reagents for decreasing or increasing the pH and suitable alkalis and acids will be readily apparent to persons skilled in the art. Of particular use are sodium carbonate, sulphuric acid, phosphoric acid, sodium hydroxide, calcium hydroxide, calcium carbonate, potassium hydroxide, potassium carbonate and combinations thereof. Adjustment of the pH during the bleaching process may contribute
20 to the enhancement or optimisation of the bleaching process.

Following bleaching, the slurry of bleached metakaolin may be filtered using any one of a number of standard techniques and may be dried to yield the brightened, bleached metakaolin product. Typical drying conditions are such that the bleached metakaolin is dried to near dryness, which corresponds to the bleached metakaolin
25 comprising about 20wt% moisture. Typically, in order to achieve near dryness, drying will take place at 50 to 600°C. The range of temperatures used in the drying process may depend on the method of drying used. For example, gas burners may be used to dry the bleached metakaolin which feed in air at high temperatures, for example 600°C. As the air becomes laden with water, the air may be rapidly cooled, for example to below 100°C.

30 The bleached metakaolin, prepared according to the invention, may be subjected to light comminution, e.g. grinding or milling. The bleached metakaolin may be treated by a known particle size classification procedure, e.g. screening and/or centrifuging, and/or by air classification to obtain particles having a desired d_{50} value. Preferably, the bleached metakaolin has a value of d_{50} in the range of 30 to 90 μ m as derived from

equivalent spherical diameter (esd) measurements. The esd measurements are made in a well known manner by sedimentation of the particulate material in a fully dispersed condition in an aqueous medium using a sedigraph 5100 machine as supplied by Micromeritics Instruments Corporation, Norcross, Georgia, USA, referred to herein as a
5 "Micromeritics Sedigraph 5100 unit". Such a machine provides measurements and a plot of the cumulative percentage by weight of particles having an esd less than given esd values. Preferably, the bleaching is reductive bleaching. Preferably the bleaching agent is used under such conditions whereby iron (III) species present on the metakaolin are reduced to a lower oxidation state such as iron (II) species. Typically, the reduced
10 iron species will be readily removed from the metakaolin by the bleaching process, due to the increased solubility of the reduced iron species in the bleaching solution when compared with the iron (III) species. The reducing bleaching agent may, for example, be selected from sodium hydrosulphite, sodium dithionite, formamidine sulphinic acid (FAS), and borohydride, for example sodium borohydride. For most metakaolins, a
15 reducing agent dose rate of about 5 parts per thousand (conventionally expressed as kg per tonne) by weight of dry metakaolin is sufficient to produce a maximum brightness value. In the case of reductive bleaching, the value of pH may be adjusted to alter the solubility of the discolouring iron species and to prevent rapid degradation of the bleaching chemicals. More specifically, the value of pH may be such that the rate of
20 hydrolysis of the bleaching chemicals is reduced or minimised.

The present invention also provides high brightness bleached metakaolins having a low relative density. More specifically, according to a second aspect of the present invention, bleached metakaolins having a relative density less than about 2.2 and an ISO brightness of greater than about 88 are provided. The bleached metakaolin may have a
25 relative density less than 2.15, for example, less than 2.10 or less than 2.05 or less than 2.0 or less than 1.95. The bleached metakaolin may, for example, have a relative density greater than about 1.90 or 1.95. Typically, the relative density of the bleached metakaolin may be in the range of about 1.95 to 2.15. The bleached metakaolin according to this aspect of the invention may have an ISO brightness greater than about
30 88.5, for example greater than 89.0 or greater than 89.5 or greater than 90.0 or greater than 90.5.

Preferably the relative density of the bleached metakaolin according to the second aspect of the invention is about 2.06, for example 2.06+/- 0.6. Preferably the low

relative density metakaolin is Opacilite™ which is commercially available from Imerys Minerals Ltd.

The ISO brightness, as expressed herein, refers to the percentage reflectance to light of a 457nm wavelength. A suitable method for measuring the ISO brightness
5 according to the present invention is set out in the test method in the Examples herein.

The metakaolin according to the second aspect of the present invention may be made according to the method of the first aspect of the present invention.

The bleached metakaolin products according to the present invention are suitable for use in a wide range of applications and in a further aspect of the present invention the
10 bleached metakaolin resulting from the first or second aspects of the present invention, may be supplied for use as a pigment additive in a filler or coating composition. For example, the bleached metakaolin is added to a paper making composition to provide filler particles for the paper making fibres or is added to a paper coating composition. Further examples include use of the bleached metakaolins according to the present
15 invention in inks, paints, ceramics, polymer products, rubber products and barrier coating compositions.

In a further aspect of the present invention, products obtained according to the methods of the present invention are also provided, namely, paper products, paper coating compositions, coated papers, inks, paints, polymers, rubber products, barrier
20 coating compositions and ceramics, all comprising the bleached metakaolin obtained according to the present invention.

Detailed Description of the Invention

25 The metakaolin

Calcined kaolins are kaolins that have been converted from the corresponding (naturally occurring) hydrous kaolin to the dehydroxylated form by thermal methods. Calcination changes the kaolin structure from crystalline to amorphous. The degree to
30 which hydrous kaolin undergoes changes in crystalline form may depend on the amount of heat to which it is subjected. Initially, dehydroxylation of the hydrous kaolin occurs on exposure to heat. At temperatures below about 850-900°C the product is considered to be virtually dehydroxylated with the resultant amorphous structure commonly being referred to as being a metakaolin. Frequently, calcination at this temperature is referred

to as partial calcination and the product may also be referred to as a partially calcined kaolin. Further heating to temperatures above about 900-950°C results in further structural changes such as densification. Calcination at these higher temperatures is commonly referred to as being full calcination and the product is commonly referred to as
5 fully calcined kaolin. Additional calcination may cause formation of mullite which is a very stable aluminium silicate.

Methods for making metakaolin are long established and well known to those skilled in the art. The furnace, kiln or other heating apparatus used to effect calcining of the hydrous kaolin may be of any known kind. A typical procedure involves heating
10 kaolin in a kiln, for example a conventional rotary kiln. Typically, the kaolin may be introduced into the kiln as an extrudate from a pug mill. As the kaolin proceeds through the kiln, typically at a starting moisture content of about 25% by weight to facilitate the extrusion of the kaolin, the extrudate breaks down into pellets as a result of the calcination process. A small amount of a binder (such as alum) may be added to the
15 kaolin to provide "green strength" to the kaolin so as to prevent the kaolin from completely breaking down into powder form during the calcination process. The temperature within the kiln should be within a specified range, typically above about 850°C but not greater than about 950°C. At approximately this temperature (i.e., 950°C), any amorphous regions of metakaolin begin to re-crystallize.

20 The period of time for calcination of kaolin to produce metakaolin is based upon the temperature in the kiln to which the kaolin is subjected. Generally, the higher the temperature, the shorter the calcination time, and conversely, the lower the temperature, the higher the calcination time.

The calcination process used may be soak calcining, i.e. wherein the hydrous
25 kaolin or clay is calcined for a period of time during which the chemistry of the material is gradually changed by the effect of heating. The calcining may for example be for a period of at least 1 minute, in many cases at least 10 minutes, e.g. from 30 minutes to five or more hours. Known devices suitable for carrying out soak calcining include high temperature ovens, rotary kilns and vertical kilns. Alternatively, the calcination process
30 may be flash calcining, wherein the hydrous kaolin is rapidly heated over a period of less than one second, e.g. less than 0.5 second. Flash calcination refers to heating a material at an extremely fast rate, almost instantaneously. The heating rate in a flash calciner may be of the order of 56,000°C per second. It is particularly preferred that the metakaolin is prepared by flash calcination, wherein the clay may be exposed to a

temperature greater than 500°C for a time not more than 5 seconds. Preferably, the clay is calcined to a temperature in the range of from 550°C to 1200°C; for microsecond periods the temperature may be as high as 1500°C. More preferably the clay is calcined to a temperature in the range of from 800°C to 1100°C; even more preferably a
5 temperature in the range of from 900°C to 1050°C; most preferably a temperature in the range of from 950°C to 1000°C. Preferably, the clay is calcined for a time less than 5 seconds; more preferably for less than 1 second; even more preferably for less than 0.5 seconds; most preferably for less than 0.1 second. Flash calcination of kaolin particles gives rise to relatively rapid blistering of the particles caused by relatively rapid
10 dehydroxylation of the kaolin. Water vapour is generated during calcination which may expand extremely rapidly, in fact generally faster than the water vapour can diffuse through the crystal structure of the particles. The pressures generated are sufficient to produce sealed voids as the interlayer hydroxyl groups are driven off, and it is the swollen interlayer spaces, voids, or blisters between the kaolin platelets which typify flash
15 calcined kaolins and give them characteristic properties.

The flash calcination process may be carried out by injecting the kaolin clay into a combustion chamber or furnace wherein a vortex may be established to rapidly remove the calcined clay from the combustion chamber. A suitable furnace would be one in which a toroidal fluid flow heating zone is established such as the device described in
20 WO 99/24360 and corresponding applications US 6334894 and US 6136740 the contents of which are herein incorporated by reference.

Any type of metakaolin is suitable for use in the bleaching process according to the present invention. Particular examples of metakaolins suitable for use in the present invention include commercially available (from Imerys) Metastar™, Metastar 402 and
25 501™, Opacilite™, Polestar 501™. According to the present invention, the metakaolin may advantageously possess 12 to 18 wt% of alumina as ascertained by acid solubility testing. A suitable method involves the extraction of soluble aluminium into concentrated nitric acid (Analar grade) and the concentration of aluminium in solution is determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using a Thermo
30 Electron Iris-AP Emission Spectrometer and 1000ppm Al Merck BDH Spectrosol standard solution.

The metakaolin product produced by the method according to the first aspect of the invention may be mixed with other pigments, fillers and extenders to obtain a blend of properties provided by the constituents of the mixture. The metakaolin according to the

second aspect of the present invention may be mixed with other pigments, fillers and extenders to obtain a blend of properties provided by the constituents of the mixture. The other pigment, filler or extender material may, for example, comprise titanium dioxide, calcium carbonate (ground or precipitated), kaolin, talc, gypsum or other known particulate mineral material, the other material being selected according to the application in which the bleached metakaolins of the present invention are to be used.

The bleaching process

The bleaching of uncalcined kaolins is a well known process and generally those processes suitable for use in bleaching uncalcined kaolins are also suitable for use in the present invention. Particularly preferred for the present invention, is the use of reductive bleaching. In general, with regard to the bleaching of kaolins, the function of reductive bleaching is to remove some or all of the surface iron staining from the kaolin in order to enhance its brightness. The procedure according to the present invention may be carried out in an aqueous suspension of the metakaolin which is usually acidic and, following bleaching, the slurry containing the bleached metakaolin may be filtered to remove the dissolved iron. For the bleaching process according to the present invention, a reducing agent dose rate of about 5 parts per thousand (which is by convention expressed as kg per tonne (kg/t)) by weight of dry metakaolin is sufficient to produce a maximum brightness value. For routine applications, this dose rate is appropriate but there will be instances apparent to the skilled person when bleaching at other dose rates will be necessary. Typically, the amount of reducing agent dose rate will be in the range of about 0.25 to 3.5kg/t, with the optimal dose rate being about 2.0 to 2.5kg/t. The amount is typically dependent on the nature of the clay being bleached and any discolouring species present. At various stages in the bleaching process it may be necessary to control the pH of the aqueous slurry. The preferred pH at the various stages of the bleaching process may vary; however, in general, prior to adding the bleaching agent, the pH of the solution is acidic and preferably less than 3. Most preferably the pH of the slurry will be 2.8 +/- 0.1. Suitable methods for measuring and adjusting the pH of the aqueous slurry will be readily apparent.

Examples of suitable bleaching agents are typically the same as those used to bleach uncalcined kaolin and will therefore be well known to those skilled in the art. The bleaching agent may be added to the aqueous metakaolin slurry either as a solid or in

aqueous solution. A particularly preferred bleaching agent is sodium hydrosulphite for example, of approximately 5% w/v or sodium dithionite, FAS or sodium borohydride.

The metakaolin used in the bleaching process according to the present invention may already have been bleached using conventional bleaching methods on uncalcined
5 kaolin.

Uses of the bleached metakaolin

The bleached metakaolin made according to the method of the present invention
10 and the high brightness, low relative density bleached metakaolin according to the second aspect of the present invention are suitable for use in a broad range of applications, all of which will be readily apparent to persons skilled in the art. Broadly, the bleached metakaolin may be employed as a pigment additive in filler and coating compositions suitable for use in paper, inks, polymers, rubbers, barrier coatings,
15 ceramics, paper coatings, paints and the like.

(a) Paper products

The term paper products should be understood to mean all forms of paper,
20 including board, card, paperboard, and the like.

The bleached metakaolins according to the present invention may be blended in various proportions with conventional filler materials, e.g. precipitated or ground calcium carbonate, kaolin and other clay minerals, metakaolin not produced according to the present invention, talc, calcium sulphate, the ingredients and composition being selected
25 according to the quality of the paper required to be produced. In general, these materials are likely to be in a slurry form when they are mixed. The bleached metakaolin of the first and second aspects of the present invention can be used in the preparation of a paper making composition or a paper coating composition. The paper making composition may typically comprise, in aqueous suspension and in addition to the
30 bleached metakaolin, cellulosic fibres and other conventional additives known in the art. A typical paper making composition would contain up to about 67% by weight of dry filler material based on the dry weight of the paper making fibres and may also contain a cationic or an anionic retention aid in an amount in the range from 0.1 to 2% by weight, based on the dry weight of the filler material. It may also contain a sizing agent which

may be, for example, a long chain alkylketene dimer, a wax emulsion or a succinic acid derivative. The composition may also contain dye and/or an optical brightening agent.

A paper coating composition will contain, in aqueous or non-aqueous suspension, and in addition to the bleached metakaolin made according to the present invention, optionally, other filler materials, a binder chosen from binders conventionally used in the art. Exemplary binders include but are not limited to adhesives derived from natural starch and synthetic binders. The formula of the paper coating composition will depend upon the purpose for which the coated paper is to be used, i.e., either for offset or gravure printing. Generally speaking, the amount of adhesive will be in the range from 3 to 35% by weight of adhesive solids, based on the dry weight of the coating. There will also be present from 0.01 to 0.5% by weight, based on the dry weight of the coating, of a dispersing agent. Sufficient alkali will generally be added to raise the pH to about 8-9. The adhesive solids may be a starch, a water dispersible synthetic resin or latex such as a styrene butadiene copolymer, a polyvinyl alcohol an acrylic, polyvinyl acetate, a butadiene-acrylonitrile copolymer, a cellulose derivative such as methyl cellulose, sodium carboxymethyl cellulose or hydroxyethyl cellulose or a proteinaceous material such as casein, animal glue or a vegetable protein. Paper coatings may include the bleached metakaolins in an amount ranging from about 3% to about 95% by weight on a dry coating basis.

Calendering is a well known process in which paper smoothness and gloss is improved and bulk is reduced by passing a coated paper sheet between calender nips or rollers one or more times. Usually, elastomer coated rolls are employed to give pressing of high solids compositions. An elevated temperature may be applied. One or more (e.g. up to about 12, or sometimes higher) passes through the nips may be applied. Methods of coating paper and other sheet materials, and apparatus for performing the methods, are widely published and well known. Such known methods and apparatus may conveniently be used for preparing coated paper. For example, there is a review of such methods published in Pulp and Paper International, May 1994, page 18 et seq. Sheets may be coated on the sheet forming machine, i.e., "on-machine," or "off-machine" on a coater or coating machine. Use of high solids compositions is desirable in the coating method because it leaves less water to evaporate subsequently. However, as is well known in the art, the solids level should not be so high that high viscosity and leveling problems are introduced. The methods of coating may be performed using apparatus comprising (i) an application for applying the coating composition to the

material to be coated; and (ii) a metering device for ensuring that a correct level of coating composition is applied. When an excess of coating composition is applied to the applicator, the metering device is downstream of it. Alternatively, the correct amount of coating composition may be applied to the applicator by the metering device, e.g., as a film press. At the points of coating application and metering, the paper web support ranges from a backing roll, e.g., via one or two applicators, to nothing (i.e., just tension). The time the coating is in contact with the paper before the excess is finally removed is the dwell time - and this may be short, long or variable.

The coating is usually added by a coating head at a coating station. According to the quality desired, paper grades are uncoated, single coated, double coated and even triple coated. When providing more than one coat, the initial coat (precoat) may have a cheaper formulation and optionally less pigment in the coating composition. A coater that is applying a double coating, i.e. a coating on each side of the paper, will have two or four coating heads, depending on the number of sides coated by each head. Most coating heads coat only one side at a time, but some roll coaters (e.g., film press, gate roll, size press) coat both sides in one pass.

Examples of known coaters which may be employed include, without limitation, air knife coaters, blade coaters, rod coaters, bar coaters, multi-head coaters, roll coaters, roll/blade coaters, cast coaters, laboratory coaters, gravure coaters, kisscoaters, liquid application systems, reverse roll coaters, curtain coaters, spray coaters and extrusion coaters.

Water may be added to the solids comprising the coating composition to give a concentration of solids which is preferably such that, when the composition is coated onto a sheet to a desired target coating weight, the composition has a rheology which is suitable to enable the composition to be coated with a pressure (e.g. a blade pressure) of between 1 and 1.5 bar.

(b) Inks

The bleached metakaolins according to the present invention are suitable for use as pigments in aqueous inks and non-aqueous inks, including, for example, gravure inks, heat-set inks, lithographic printing inks, and newsprint inks. Depending on the final applications of the ink, the ink may further comprise at least one component chosen, for example, from resins, such as vinyl resins; polymers; additives, such as rheology

modifiers, surfactants, and drying accelerating agents such as sodium lauryl sulfate, N,N-diethyl-m-toluamide, cyclohexylpyrrolidinone and butyl carbitol; fillers; diluents; humectants, such as ethylene glycol, propylene glycol, diethylene glycols, glycerine, dipropylene glycols, polyethylene glycols, polypropylene glycols, amides, ethers, carboxylic acids, esters, alcohols, organosulfides, organosulfoxides, sulfones, alcohol derivatives, carbitol, butyl carbitol, cellosolve, ether derivatives, amino alcohols, and ketones; and biocides, such as benzoates, sorbates, and isothiazolones. The ink product can further comprise at least one additional pigment chosen from those conventionally used in the art. The amount of bleached metakaolin in a given ink can vary greatly, based on the formulation of the ink, as would be apparent to one of ordinary skill in the art. For example, the bleached metakaolin can comprise from 5%-45% by weight of the ink as formulated.

(c) Rubber products

The bleached metakaolins according to the present invention may be incorporated into a rubber composition. The metakaolin may, for example, be used as a filler or an extender in the rubber composition. The composition comprising the metakaolin prepared according to the present invention can provide the benefits of resin extension, reinforcement and increased hardness of the rubber composition. The rubber product disclosed herein comprises at least one rubber chosen from natural rubbers and synthetic rubbers. For example, sulphur-vulcanisable rubbers, which can be used for the manufacture of tyre treads. Examples of the synthetic rubbers, which may be used in the present invention, include, but are not limited to, styrene-butadiene rubber (SBR), vinylstyrene-butadiene rubber (VSBR), butadiene rubber (BR), and neoprene rubber or polyisoprene. The SBR may be emulsion SBR (E-SBR) or solution SBR (S-SBR). The VSBR may be solution VSBR (S-VSBR). Examples of the BR include, cis-1,3-polybutadiene rubber and cis-1,4-polybutadiene rubber. An example of the natural rubbers, which the bleached metakaolins of the present invention can be used in is Standard Malaysian natural rubber. The rubber products may further comprise at least one additive chosen from conventional additives used in the art, for example, extender oils and mineral and synthetic fillers. The rubber can include an amount of the bleached metakaolin to about 35% by weight as formulated.

(d) Paints

The bleached metakaolins according to the present invention may be used in paints, such as an aqueous or non-aqueous industrial coating, architectural paint, deco
5 paint, or art paint, comprising, in an appropriate medium, the bleached metakaolin of the present invention. The bleached metakaolins disclosed herein can serve, for example, as a gloss control agent pigment in the paint. The bleached metakaolin will generally be present in an amount less than the critical pigment volume. However, the bleached metakaolins of the present invention can also be present in higher pigment volume
10 concentrations, such as for example in the range of 1% to 80% by weight on a dry film basis. The paint will typically further comprise at least one component chosen from binders, such as polymeric binders, for example, water dispersible binders chosen, for example, from polyvinyl alcohol (PVA) and latex; and additives conventionally used in paints, chosen, for example, from surfactants, thickeners, biocides, defoamers, wetting
15 agents, dispersants, and coalescents. The paint may comprise at least one additional pigment chosen, for example, from TiO_2 and calcium carbonate.

(e) Polymer products

20 The bleached metakaolins according to the present invention may be incorporated in polymer products and are typically present at a concentration of up to 60% by weight of the polymer as compounded and up to 30% by weight of the final polymer article. In addition to its role as a pigment, the bleached metakaolin can be used both for resin extension (i.e., filling), TiO_2 extension, and reinforcement of the polymer. The polymer
25 product comprises at least one polymer resin. The term resin means a polymeric material, either solid or liquid, prior to shaping into a plastic article. The at least one polymer resin is one which, on cooling (in the case of thermoplastic plastics) or curing (in the case of thermosetting plastics), can form a plastic material. The at least one polymer resin, can be chosen, for example, from polyolefin resins, polyamide resins, polyester
30 resins, engineering polymers, allyl resins, thermoplastic resins, and thermoset resins.

The bleached metakaolins of the present invention may be combined with a polymer resin to form a polymer composition from which a shaped article is subsequently formed. "Polymer resin" is the general term used in the plastics art to denote a polymeric material (solid or liquid) prior to shaping into a plastic article. In the case of thermoplastic

polymers, the polymer resin is melted (or otherwise softened) prior to formation of an article usually, by a moulding process, and the polymer will not normally be subjected to any further chemical transformations. After formation of the shaped article, the polymer resin is cooled and allowed to harden. In the case of thermosetting polymers, the
5 polymer resin is in a precursor state which, after shaping, is cured to obtain the final polymeric article. In the curing stage, chemical crosslinks are formed. The bleached metakaolins of the present invention are suited for use with polymer resins which are thermoplastic in nature or to polymer resins in which the resin is thermosetting.

The polymer resin composition may be made by methods which are well known in
10 the art generally in which the bleached metakaolin and the polymer resin are mixed together in suitable ratios to form a blend (so-called "compounding"). In general, the polymer resin should be in a liquid form to enable the particles of the filler to be dispersed therein. Where the polymer resin is solid at ambient temperatures, therefore, the polymer resin will need to be melted before the compounding can be accomplished. In
15 some embodiments, the bleached metakaolin may be dry blended with particles of the polymer resin, dispersion of the particles in the resin then being accomplished when the melt is obtained prior to forming an article from the melt, for example in an extruder itself.

In embodiments of the invention, the polymer resin and the bleached metakaolin and, if necessary, any other optional additives, may be formed into a suitable
20 masterbatch by the use of a suitable compounder/mixer in a manner known per se, and may be pelletized, e.g. by the use of a single screw extruder or a twin-screw extruder which forms strands which may be cut or broken into pellets. The compounder may have a single inlet for introducing the filler and the polymer together. Alternatively, separate inlets may be provided for the filler and the polymer resin. Suitable compounders are
25 available commercially, for example from Werner & Pfleiderer. Examples of suitable additives include pigments other than those according to the present invention, antioxidants, processing aids, light stabilisers and glass fibre.

The polymer resin compositions incorporating the bleached metakaolins can be processed to form, or to be incorporated in, articles of commerce in any suitable way.
30 Such processing may include compression moulding, injection moulding, gas-assisted injection moulding, calendaring, vacuum forming, thermoforming, extrusion, blow moulding, drawing, spinning, film forming, laminating or any combination thereof. Any suitable apparatus may be used, as will be apparent to one of ordinary skill in this art.

The articles which may be formed from the polymer compositions are many and varied. Examples include films, engineering thermoplastics and PVC cables.

(f) Ceramics

5

The bleached metakaolin according to the present invention may be incorporated into ceramic forming compositions. Ceramic articles are generally formed from a wet high solids composition which comprises a blend of various particulate ingredients which includes kaolinitic clays, i.e. clays which contain the mineral kaolinite. Often, fluxing materials such as china stone, feldspar or nepheline syenite and at least one silica containing material such as quartz or flint are included in such compositions. For the production of bone china the composition will also contain a substantial proportion of ground calcined animal bone. The composition may also include minor proportions of other ingredients such as calcium carbonate, dolomite and talc. The proportions of the various ingredients used in the composition will vary according to the properties in the fired ceramic article. Prior to firing the ceramic forming composition it is shaped and dried. The ceramic forming composition will need to have sufficient plasticity to enable it to be shaped and it must also possess sufficient strength in its unfired or "green" state to permit a certain amount of handling without loss of its integrity and shape.

20

(g) Barrier coatings

The bleached metakaolins according to the present invention may be incorporated into barrier coating compositions which comprise a slurry comprising the bleached metakaolin. Typically the solids content of the slurry ranges from about 45% to about 70% by wt. Barrier coatings are generally useful in imparting to paper, moisture resistance, moisture vapour resistance, and resistance to grease, oil, air and the like. The amount of binder in the barrier coating may be in the range of about 40% to 50% by wt.

30

Examples

Embodiments of the present invention will now be described by way of example only with reference to the following examples.

35

Test Methods

Brightness (ISO)

5 The ISO brightness is the percentage of light reflected by a body compared to that reflected by a perfectly reflecting diffuser measured at 457nm. A Datacolour Elrepho fitted with two tungsten lamps, a gloss shield and a range of filters which includes one at a nominal setting of 457nm and one at a nominal setting of 571nm was used.

10 A test surface is produced by pulverizing a dried material, for example using an Imerys pulveriser, to disperse it completely then compressing it under a pressure of 1.2kg cm⁻² to form a powder tablet. Drying is carried out in an oven and dryness of the sample is denoted by the absence of condensation on a piece of cool plate glass when placed in close proximity to the surface of the sample which has been removed from the oven. Suitable drying ovens include the forced circulation type which are capable of maintaining a temperature of 80°C to within 5°C.

15 The reflectance values of this tablet are measured at two wavelengths in the visible spectrum. The measurements were made with the ultraviolet component excluded. The primary standard adopted was an ISO level 2 reflectance standard, supplied and calibrated by Physikalisch-Technische Bundesanstalt (P.T.B.) West Germany. A working standard, in this case a ceramic tile, was used to calibrate the
20 photometer for brightness measurements which had been calibrated previously against the level 2 standard.

Yellowness (YEL)

25 The yellowness was measured according to the procedure described above for the brightness measurements. The yellowness is reported as the value obtained when the reflectance at 457nm is subtracted from the reflectance at 571nm.

Whiteness (WHI)

30 The whiteness was measured according to the CIE standard codified by ISO 11475:1999 and Determination of CIE whiteness, D65/10 degrees (outdoor daylight).

Reductive bleaching of a metakaolin

Preparation of the bleaching reagent solution

5 An appropriate amount of sodium carbonate or sodium hydroxide was added to deionised water to raise its pH to 12. The mixture was stirred gently to ensure dissolution. Stirring was continued whilst 5.0g +/- 0.1g of sodium hydrosulphite powder was added. The rate of stirring was such that air entrainment was kept to a minimum. Mixing was continued for 10 minutes and the solution transferred to a burette. It is
10 recommended that the solution should not be stored for more than about 2 hours unless suitable precautions are taken against the effects of oxidation, for example by covering the surface with a light oil.

Preparation and bleaching of the slurry

15 20g +/- 0.1g of the metakaolin was added to 100ml of deionised water in an homogeniser pot or beaker. Dispersion of the metakaolin was carried out for about 1 minute with the homogeniser or at least 3 minutes with the stirrer. The aqueous sample was mixed to homogeneity with the bench stirrer or alternatively rotating rollers and the
20 density measured. The pH of the slurry was measured using a pH meter buffered to pH 4 and adjusted to pH 2.8 +/- 0.1 with either 4% w/v sulphuric acid or 5% w/v sodium carbonate and stirring. The sodium hydrosulphite solution was added to the slurry in an amount equivalent to 5 parts per thousand. For 20g of dry weight equivalent of metakaolin this equates to 0.1g of powder or 2ml of 5% w/v solution. Thorough mixing
25 was carried out in order to avoid air entrainment. The pH of the slurry was readjusted to 2.8 +/- 0.1 using 4%w/v sulphuric acid. After a further 2 minutes the pH was again readjusted to 2.8 +/- 0.1. The slurry was allowed to stand for approximately a further 8 minutes without stirring. The pH was then adjusted to between 4 and 4.5 with 5% w/v sodium carbonate, whilst stirring with a rod to ensure complete mixing, followed by
30 immediate filtration. The sample was dried at 80°C and tested.

Table 1 compares the metakaolins Metastar 402 TM and 501 TM before and after bleaching. The bleaching techniques, carried out according to the procedure above, resulted in a significant increase in brightness and whiteness and a corresponding significant decrease in yellowness.
35

Table 1

Sample		ISO	YEL	WHI
M'STAR 501	Feed	84.8	6.9	71.2
	Bleached	86.1	6.3	73.5
M'STAR 402	Feed	76	8.6	57.2
	Bleached	80.8	5	69.1

- 5 Table 2 illustrates data obtained for the flash calcined metakaolin, Opacilite TM, which is commercially available from Imerys. The procedure was the same procedure as that outlined above for the Metastar samples except a range of doses of bleaching agent were used. In Table 2, Phos is an abbreviation for phosphoric acid and Dose corresponds to the dose of sodium hydrosulphite in kg per tonne of clay in suspension.
- 10 The acids were used for adjusting the pH.

Table 2

Opacilite	Dose	Acid	ISO	YEL	WHI
(1) Feed			86.6	3.6	79
Bleached	1	Phos	86.8	3.5	79.3
Bleached	2	Phos	87	3.3	80
Bleached	3	Phos	87.1	3.2	80.2
Bleached	5	Phos	87.2	3.2	80.4
Bleached	3	H ₂ SO ₄	87.2	3.1	80.4
(2) Feed			89.2	2.9	82.9
Bleached	1	Phos	88.5	2.7	82.5
Bleached	2	Phos	88.6	2.7	82.7
Bleached	3	Phos	88.8	2.7	82.9
Bleached	5	Phos	88.6	2.7	82.6
Bleached	3	H ₂ SO ₄	89.6	2.7	83.7
(3) Feed			87.6	3.1	80.7
Bleached	3	H ₂ SO ₄	88.4	2.7	82.5
(4) Feed			88	2.8	81.7
Bleached	3	H ₂ SO ₄	88.7	2.6	82.8

Conclusions

5 The methods of the present invention result in metakaolins with increased brightness, increased whiteness and decreased yellowness and are suitable for producing high brightness, low relative density, bleached metakaolins.

Without wishing to be bound by a particular theory, it is considered that during the formation of metakaolin, the structure of the kaolin particles is disrupted allowing the lattice iron to become, at least partially, accessible to any subsequent bleaching
10 conditions. Also, any residual surface iron may be converted to iron (II) species, which will be readily removed by the bleaching process according to the present invention.

Claims

1. A method of increasing the brightness of a metakaolin comprising bleaching the metakaolin.
2. A method according to claim 1, wherein the metakaolin is in the form of a dispersed aqueous slurry.
3. A method according to claim 1 or 2, wherein the metakaolin is bleached using a reductive bleaching agent.
4. A method according to claim 3, wherein the reductive bleaching agent is selected from sodium dithionite, sodium hydrosulphite, formamidine sulphinic acid, borohydride and a combination of formamidine sulphinic acid and borohydride.
5. A method according to claim 4, wherein the reductive bleaching agent is sodium hydrosulphite.
6. A method according to claim 4, wherein the reductive bleaching agent is formamidine sulphinic acid.
7. A method according to claim 4, wherein the reductive bleaching agent is sodium dithionite.
8. A method according to claim 4, wherein the reductive bleaching agent is borohydride.
9. A method according to claim 4, wherein the reductive bleaching agent is a combination of formamidine sulphinic acid and borohydride.
10. A method according to claim 8 or 9, wherein the borohydride is sodium borohydride.
11. A method according to any one of claims 3 to 10, wherein the bleaching agent is in solid or liquid form.

12. A method according to any of claims 3 to 11 wherein the amount of reductive bleaching agent is about 0.25 to 3.5kg per tonne of metakaolin.
- 5 13. A method according to the preceding claim wherein the amount of reductive bleaching agent is about 2.0 to 2.5kg per tonne of metakaolin.
14. A method according to the preceding claim wherein the amount of reductive bleaching agent is about 2.5kg per tonne of metakaolin.
- 10 15. A method according to any one of claims 2 to 14, wherein following bleaching, the bleached metakaolin is filtered and dried.
16. A method according to claim 15, wherein drying is carried out at a temperature range of 50 to 600°C.
- 15 17. A method according to claim 15 or 16, wherein following drying, the bleached metakaolin is subjected to comminution.
- 20 18. A method according to the preceding claim wherein the bleached metakaolin is ground or milled.
19. A method according to any one of claims 15 to 18 wherein the d_{50} of the bleached metakaolin is in the range of 30 to 90 μ m.
- 25 20. A method according to any one of claims 1 to 19, wherein prior to bleaching the metakaolin, the pH of the metakaolin or slurry of metakaolin is adjusted.
21. A method according to any one of claims 1 to 20, wherein the pH of the metakaolin or slurry of metakaolin is adjusted after bleaching the metakaolin.
- 30 22. A method according to claim 20 or 21, wherein the pH is made more acidic.
23. A method according to claim 22 wherein the pH lies in the range of 2 to 3.

24. A method according to the preceding claim wherein the pH is about 2.8.
25. A method according to claims 22 to 24, wherein the pH is made more acidic using
5 any of phosphoric acid, sulphuric acid or a combination thereof.
26. A method according to claim 20 or 21, wherein the pH is made more alkaline.
27. A method according to any one of claims 22 to 25 wherein following acidification the
10 pH is made more alkaline.
28. A method according to either of claims 26 or 27 wherein the pH is made more
alkaline using any of sodium carbonate, sodium hydroxide, calcium hydroxide, calcium
carbonate, potassium hydroxide, potassium carbonate or a combination thereof.
15
29. A method according to any one of the preceding claims wherein the bleached
metakaolin is at least 0.3 ISO units brighter than the metakaolin prior to bleaching.
30. A method according to the preceding claim wherein the bleached metakaolin is at
20 least 0.5 ISO units brighter than the metakaolin prior to bleaching.
31. A method according to the preceding claim, wherein the bleached metakaolin is at
least 1.0 ISO units brighter than the metakaolin prior to bleaching.
- 25 32. A method according to the preceding claim, wherein the bleached metakaolin is at
least 2.0 ISO units brighter than the metakaolin prior to bleaching.
33. A method according to the preceding claim wherein the bleached metakaolin is at
least 3.0 ISO units brighter than the metakaolin prior to bleaching.
30
34. A method according to the preceding claim wherein the bleached metakaolin is at
least 5.0 ISO units brighter than the metakaolin prior to bleaching.

35. A method according to any one of the preceding claims wherein the metakaolin is a flash calcined kaolin or a soak calcined kaolin.
36. A method according to any one of the preceding claims wherein the metakaolin
5 possesses 12 to 18 wt% of alumina as ascertained by acid solubility testing.
37. A method according to any one of the preceding claims wherein the metakaolin is selected from Metastar TM, Metastar 402 TM, Metastar 501 TM, Opacilite TM.
- 10 38. A bleached metakaolin obtained according to the method of any one of the preceding claims.
39. A method according to any one of claims 1 to 37, further comprising incorporating the bleached metakaolin in to any one of a paper composition, a paper coating composition,
15 an ink composition, a polymer composition, a rubber product, a barrier coating composition, a ceramic composition or a paint composition.
40. A method according to any one of claims 1 to 37, further comprising combining the bleached metakaolin with at least one component chosen from resins, polymers,
20 additives, fillers, diluents, humectants, biocides and additional pigments in an ink making process.
41. A method according to any one of claims 1 to 37, further comprising blending the bleached metakaolin with one or more of precipitated or ground calcium carbonate,
25 kaolin, clay minerals other than kaolin, talc, calcium sulphate, cellulosic fibres, a retention aid, and a sizing agent in a paper making process.
42. A method according to any one of claims 1 to 37, further comprising blending the bleached metakaolin with one or more binders, surfactants, thickeners, biocides,
30 defoamers, wetting agents, dispersants and coalescents and an additional pigment in a paint making process.

43. A method according to any one of claims 1 to 37, further comprising mixing the bleached metakaolin with a binder into an aqueous or non-aqueous medium to form a suspension suitable for use as a paper coating composition.
- 5 44. A method according to claim 43, further comprising coating a paper product with said paper coating composition followed by calendaring of the coated product.
45. A method according to any one of claims 1 to 37, further comprising combining the bleached metakaolin with a rubber and optionally at least one additive chosen from
10 extender oils and mineral and synthetic fillers in a rubber making process.
46. A method according to any one of claims 1 to 37, further comprising combining the bleached metakaolin with a binder to form a mixture suitable for use as a barrier coating composition.
15
47. A method according to any one of claims 1 to 37, further comprising incorporating the bleached metakaolin into a ceramic forming composition.
48. A method according to claim 47 further comprising shaping, drying and firing the
20 ceramic forming composition to form a ceramic article.
49. A method according to any one of claims 1 to 37 further comprising incorporating the bleached metakaolin in a polymer resin composition.
- 25 50. A method according to claim 49 further comprising forming the polymer resin composition into an article.
51. Use of the bleached metakaolin obtained according to claim 38 in any one of a paper composition, a paper coating composition, a paint composition, a polymer composition,
30 an ink composition, a ceramic composition, a barrier coating composition or a rubber product.
52. An ink obtained according to the method of claim 39 or 40.

53. A paper product obtained according to the method of claim 39 or 41.

54. A paint obtained according to the method of claim 39 or 42.

5 55. A paper coating composition obtained according to the method of claim 39 or 43.

56. A calendered paper product obtained according to the method of claim 44.

57. A rubber product obtained according to the method of claim 39 or 45.

10

58. A barrier coating composition obtained according to the method of claim 39 or 46.

59. A ceramic forming composition obtained according to the method of claim 39 or 47.

15 60. A ceramic article obtained according to the method of claim 48.

61. A polymer resin obtained according to the method of claim 39 or 49.

62. An article obtained according to the method of claim 50.

20

INTERNATIONAL SEARCH REPORT

Interr | Application No
PCT/GB2005/001823

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B33/40 C09C1/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01B C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, INSPEC, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X A	US 5 393 340 A (SLEPETYS ET AL) 28 February 1995 (1995-02-28) column 1, lines 41-59; example 1; table 3	38 1-37, 39-62
X A	WO 99/67335 A (GINN, MICHAEL, W) 29 December 1999 (1999-12-29) page 10, line 27 - page 11, line 3 page 13, line 31 - page 14, line 33 ----- -/--	38 1-37, 39-62

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Inter Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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